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(56) Documents Cited

EP 0434085 A2 EP 0432649 A1 US 4576705 A

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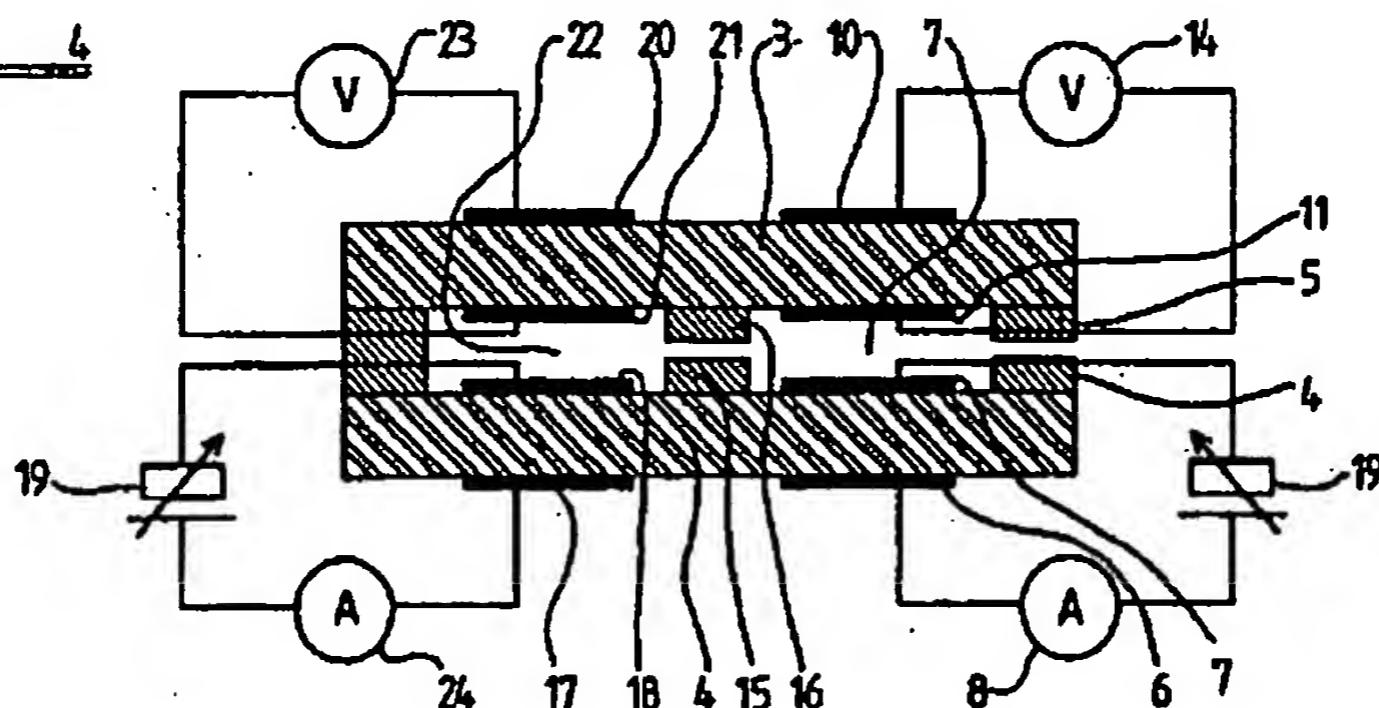
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(54) Multi-component gas analysis apparatus

(57) The apparatus which measures the concentration of two or more gases such as oxygen and nitric oxide in a gas mixture has at least two compartments 7 and 22 in which the most easily reduced gas is reduced in the first compartment 7 and the next easily reduced gas is reduced in the second compartment 22 and so on until all the gases of interest have been reduced. The reduction is carried out by applying a voltage from sources 9, 19 between electrodes 6, 7 and 17, 18 located on opposite sides of solid electrolyte 4. A voltage of 100 - 200 mV is used for oxygen, 250 - 300 mV for nitric oxide and 800 mV for SO₂. The current, as measured by ammeters 8 and 24, required to electrochemically reduce each gaseous component being measured in the gas mixture is directly proportional to the concentration of that gas in the mixture. Gas partial pressures in the cavities 7, 22 can be monitored and the reductions controlled by solid electrolyte gauge sensors 10, 3, 11 and 20, 3, 21.

FIG 4



At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1990.

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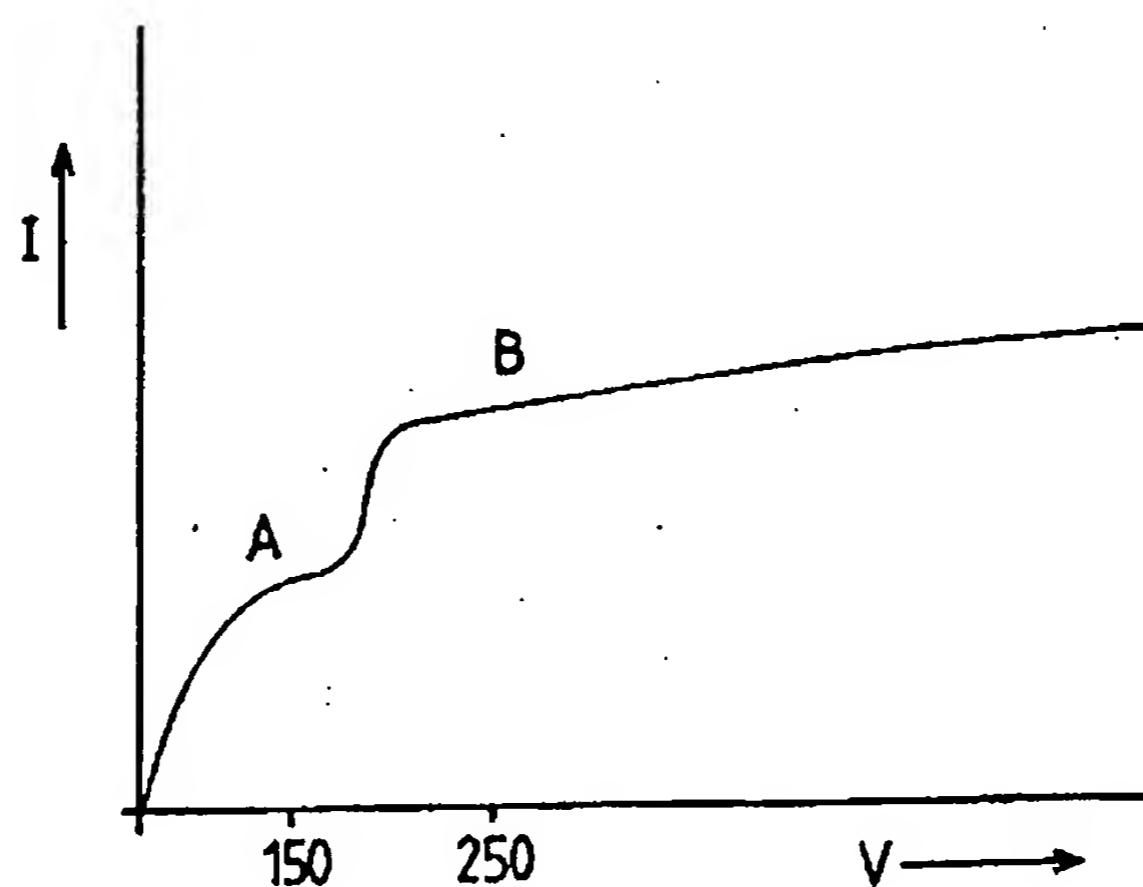
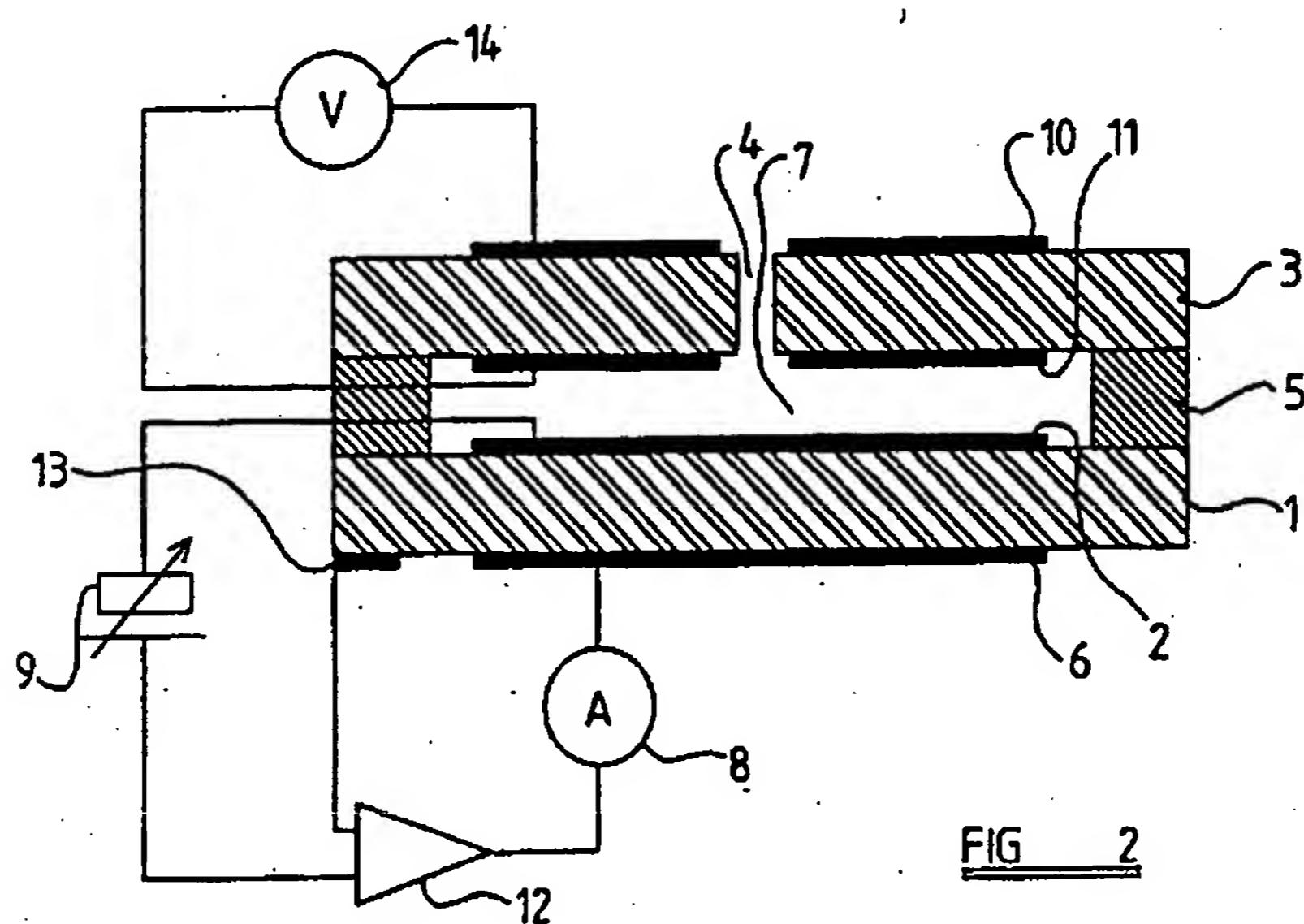
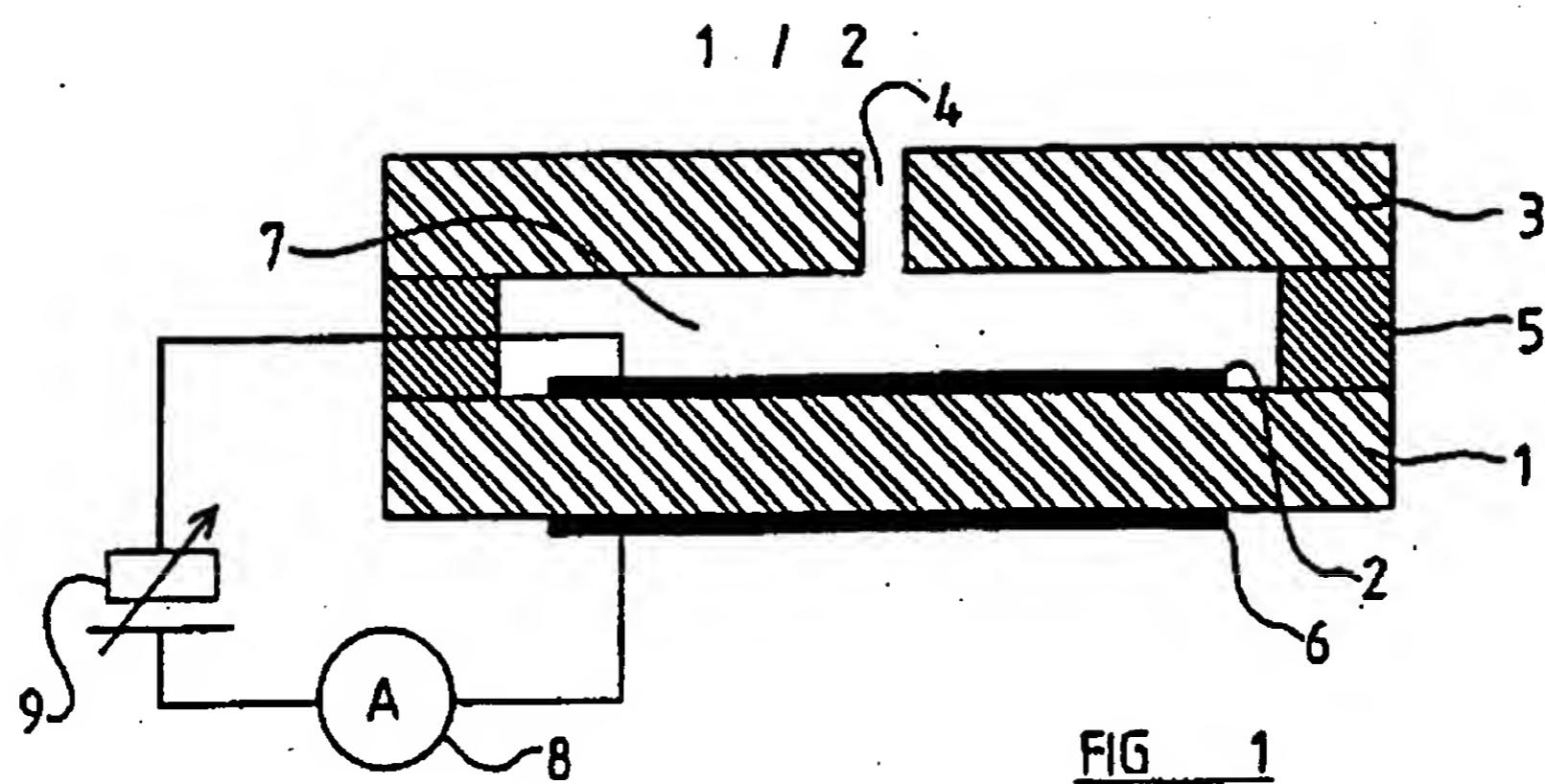
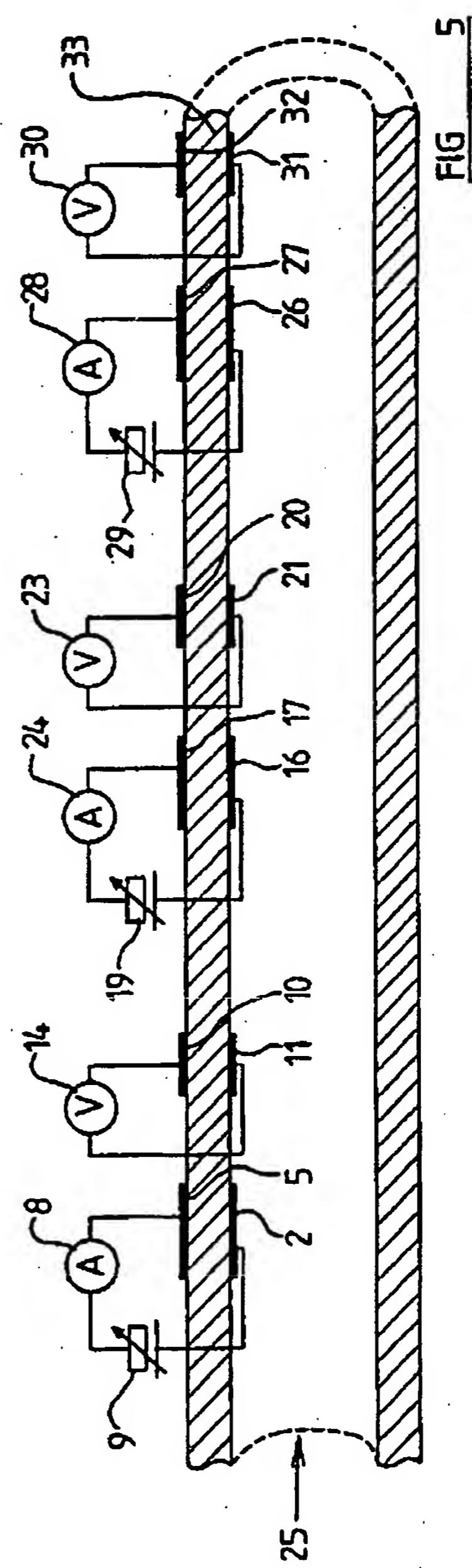
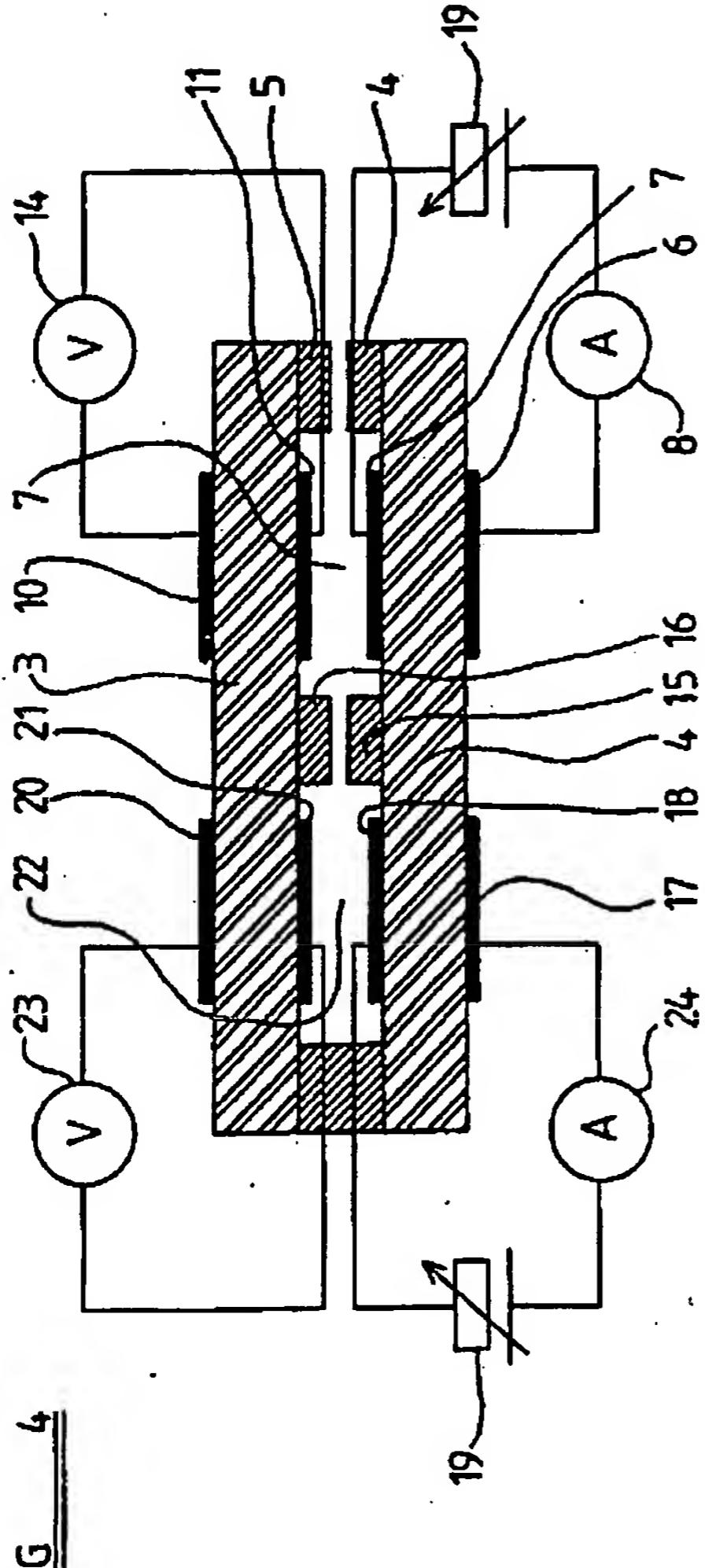


FIG 3



PATENTS ACT 1977

Multi-component Gas Analysis Apparatus

This invention relates to the measurement of oxygen containing gas concentration.

Nitric oxide and several other nitrogen oxides belonging to the group called NO_x are toxic gases that produce acid rain among other problems. They are produced primarily by the wide range of combustion processes used in modern society. There is a need for a sensor for detecting NO_x that can withstand the high temperatures found in the exhaust outlets of these combustion processes. Sensors constructed from solid electrolytes are robust and ideally suited to high temperature operation which means that they can be used directly in hot exhaust gases as part of a feed-back control loop.

Zirconia is a solid electrolyte that conducts oxygen ions and has been widely used in two basic classes of oxygen sensor: the potentiometric sensor and the amperometric sensor. Figure 1 illustrates the principles of the amperometric sensor. Two electrodes, 2 and 6 are deposited into a zirconia disc 1. Electrode 2 is covered by another disc 3 of any suitable material and separated from this electrode by a suitable separating ring 5. A diffusion pore 4 within disc 3 or ring 5 restricts the flow of gas to electrode 2. Oxygen is electrochemically pumped from electrode 2 to electrode 6 by the application of a current from power source 9. When the applied voltage from power source 9 is less than about 200mV only oxygen is reduced at cathode 2. The pumping current that results and is measured by ammeter 8 is directly proportional to the oxygen concentration and can therefore be used to measure this concentration.

When applied voltage 9 is between about 200 and 300mV nitric oxide is also reduced. The extra current that flows is directly proportional to the NO concentration.

Figure 2 illustrates an extension of the basic amperometric sensor called the pump-gauge sensor. The covering disc 3 is now also made from a solid electrolyte and two extra electrodes 10 and 11 have been added. A pumping current is passed through electrodes 2 and 6 as before and the cell consisting of electrodes 2 and 6 and the electrolyte disc 3 is called the gauge cell. No current flows through the gauge cell so no overvoltages develop on the gauge electrodes 10 and 11. The voltage on the gauge cell measured by voltmeter 14 is a Nernst voltage that reflects the difference in oxygen partial pressure between electrodes 10 and 11. The oxygen partial pressure within the enclosed volume 7 can therefore be determined. Figure 3 shows how the pump current increases as the gauge voltage increases when the sensor is in a gas mixture containing oxygen, nitric oxide and an inert gas. The plateau in pump current at point A is due to oxygen reduction and that at B due to nitric oxide and oxygen reduction. The obvious way to measure NO concentration is to step between the two gauge voltages represented by points A and B in Figure 3 and measure the difference in pump current. One difficulty with this idea is that it takes several minutes for the pump current to reach steady state due to capacitive effects in the electrodes. The second difficulty is that if the NO concentration is much smaller than the oxygen concentration it is very difficult to measure the relatively small change in pumping current due to NO reduction.

Accordingly, in order to overcome the above difficulties, one aspect of the present invention provides a method a method of detecting the presence of a particular gas in a gas mixture comprising the steps of exposing at

least a first electrode to a volume of gas in a control chamber; exposing at least a second electrode to a gas mixture outside the control chamber; selecting and applying a predetermined voltage across the first and second electrodes, which predetermined voltage allows detection of a selected particular gas in the gas mixture.

Further, another aspect of the present invention provides a sensor for detecting the presence of a plurality of gases comprising: a plurality of control chambers each enclosing a volume of gas and having an associated electrode exposable to the respective volume of gas in the respective control chamber; and at least one electrode exposable to a volume of gas outside the control chambers, wherein the application of a selected and predetermined voltage across each electrode associated with a control chamber and the at least one electrode exposable to the volume of gas outside the control chambers detects a particular selected gas in the volume of gas outside the control chambers.

In order that the present invention may be more readily understood, embodiments thereof will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is diagrammatic cross-section of amperometric sensor;

Figure 2 is diagrammatic cross-section of a pump-gauge sensor;

Figure 3 is a graph showing the relationship between pump current and gauge voltage;

Figure 4 is a diagrammatic cross-section of an embodiment of the present invention; and

Figure 5 is a diagrammatic cross-section of another embodiment of the present invention.

One embodiment of the invention consists of a device with two compartments 7 and 22 separated by dividing

partition 15 through which a small diffusion pore 16 is placed as illustrated in Figure 4. Power supply 9 is set to a value typically between about 100 and 200mV so that electrode 2 reduces oxygen only. The pump current measured by ammeter 8 therefore indicates the oxygen concentration. Gas containing very little free oxygen is passed to the second compartment 22 and power supply 19 is set to supply a slightly higher pumping voltage (typically 250 to 300mV) which allows the reduction of NO. The pump current through electrodes 17 and 18 as measured by ammeter 24 is therefore proportional to the NO concentration. The combined sensor therefore produces two signals, one for oxygen concentration and one for NO concentration with relatively little interference between the two. This increases the sensitivity of the device to NO and because the electrode voltages do not undergo large changes, the slow response due to electrode capacitance effects is removed and sensor response should approach the order of 1 second.

Both compartments in Figure 4 have gauge electrodes: electrodes 10 and 11 for compartment 7 and electrodes 20 and 21 for compartment 22. These are included so that the sensor control circuit can avoid the effects of any overvoltages that could develop on electrodes 2 and 6 in compartment 7 and 17 and 18 in compartment 22. If the gauge voltages are used to control the pumping voltages in each compartment using a suitable control circuit the oxygen activity within the compartments will be more accurately maintained at the desired values.

The principle of the above sensor can be extended to any oxygen containing gas simply by adjusting the gauge voltages in the two compartments. The principle can also be extended to detect more than two gases simultaneously. Figure 5 shows an alternative layout of the device which has also been extended to detect 3 gases simultaneously. The gas is passed at a fixed rate down solid electrolyte

tube 33 in the direction shown by arrow 25. The gauge voltage on the second stage measured by voltmeter 23 is higher than that on the first stage measured by voltmeter 14 and the third stage has the highest gauge voltage measured by voltmeter 30. For instance to detect O₂, NO and SO₂ the first gauge voltage, as measured by voltmeter 14, would be set to about 150m V by the application of a suitable voltage from power source 9 to electrodes 2 and 6 such that about 99.9% of the oxygen entering tube 33 is reduced at electrode 2. The resultant current measured by ammeter 8 is a measure of the O₂ concentration. Power source 19 supplies a higher voltage to electrodes 17 and 18 so that NO is reduced at electrode 18 and the difference in potential between electrodes 21 and 20 as measured by voltmeter 23 becomes about 300mV. SO₂ is reduced in the third stage at electrode 26 by the application of a voltage from power source 29 which sets the potential measured by voltmeter 30 to about 800mV. Thus, three signals, one for each gas, would be obtained from the device.

The principle of the above device could be extended to gases other than oxygen. For instance if an electrolyte in which chlorine ions were most mobile was used, the first compartment could be used to reduce chlorine and the subsequent compartments could be used to reduce chlorine containing gases such as HCl. It is also possible that different compartment could include pump cells using different electrolytes. For instance sulphur dioxide has been shown to interfere with the performance of zirconia amperometric sensors. If the sulphur dioxide was removed in the first compartment using a sulphate solid electrolyte any subsequent compartment using zirconia would be protected. This would also add to the range of gases that could be detected by the one device.

A fifth electrode through which negligible current flows called a reference electrode (13 in Figure 2) could be added to the pump cell of any compartment for the purposes of determining the overvoltages on either or both pumping electrodes. This additional information could be used to aid the analysis of the gas.

Catalytic layers could also be included to aid the detection of different gases. For instance the oxygen potential required to reduce carbon dioxide to carbon monoxide or carbon is very similar to that required to reduce steam to hydrogen. The device as described above could accurately distinguish between CO_2 and H_2O . However, if the second compartment contained a catalyst layer that promoted the reduction of CO_2 but not that of H_2O then the second compartment would produce a current signal more representative of the CO_2 concentration and the third compartment would reduce H_2O almost exclusively. Careful choice of sensor operating temperature will also help in achieving gas concentration signals that have the least cross-sensitivity.

CLAIMS:

1. A method of detecting the presence of a particular gas in a gas mixture comprising the steps of exposing at least a first electrode to a volume of gas in a control chamber;

exposing at least a second electrode to a gas mixture outside the control chamber;

selecting and applying a predetermined voltage across the first and second electrodes, which predetermined voltage allows detection of a selected particular gas in the gas mixture.

2. A sensor for detecting the presence of a plurality of gases in a gas mixture comprising:

a plurality of control chambers each enclosing a volume of gas and having an associated electrode exposable to the respective volume of gas in the respective control chamber; and

at least one electrode exposable to a volume of gas outside the control chambers, wherein the application of a selected and predetermined voltage across each electrode associated with a control chamber and the at least one electrode exposable to the volume of gas outside the control chambers detects a particular selected gas in the gas mixture.

3. A sensor according to Claim 2, wherein the control chambers are provided in series and the voltage applied across each electrode associated with a control chamber and the at least one electrode exposable to the volume of gas outside the control chambers increases from one control chamber to the next.

4. A sensor according to Claim 3, wherein each control chamber is separated by a diffusion barrier.
5. A sensor according to any one of Claims 2 to 4, wherein the sensor is a polarographic sensor for oxygen-containing gases such as NO or SO₂.
6. A sensor according to any one of Claims 2 to 5, wherein the sensor is a zirconia amperometric sensor.
7. A sensor according to anyone of Claims 2 to 6 for measuring the concentration of a particular gas in a gas mixture, which sensor consists of at least two control chambers, the first connected by a flow control device to a gas mixture being analyzed to reduce electrochemically the particular gas only by the application of a suitable electrochemical pumping voltage to the electrodes on either side of an ion conducting solid electrolyte membrane making up at least part of the wall of the control chamber, the remaining control chambers being connected to the immediately preceding control chamber by a flow control device and which are set up to progressively electrochemically reduce the increasingly stable gases in the gas mixture so that the device produces current signals, the signal from the first control chamber being proportional to the concentration of the particular gas in the gas mixture in the first control chambers and the signals from the succeeding control chamber being proportional to the concentration of the gases being reduced in those control chambers.
8. A sensor according to any one of Claims 2 to 7, wherein a gauge and a pump cell are used in each control chamber in order to bypass the difficulties caused by

variable overvoltages on the electrodes and thereby improve the operation of the sensor.

9. A sensor according to any one of Claims 2 to 8, wherein oxygen ions are mobile in the solid electrolyte.

10. A sensor according to any one of Claims 2 to 8, wherein ions other than oxygen are mobile in the electrolyte.

11. A sensor according to any one of Claims 2 to 10, wherein a reference electrode is added to one or more of the control chambers in order to enhance the sensing ability of the sensor.

12. A sensor according to any one of Claims 2 to 11, whereby different materials are used for constructing each of the control chambers in order to increase the selectivity or sensitivity of the sensor to the gases of interest and to increase the range of gases that can be detected by a single sensor device.

13. A sensor according to any one of Claims 2 to 12, wherein catalytic layers are added to any part of any control chamber in the sensor in order to increase the selectivity or sensitivity of the device to the gases of interest and to increase the range of gases that can be detected by a single device.

14. A sensor according to any one of Claims 2 to 13, wherein a heating device is incorporated so that the device can be raised to a suitable operating temperature.

15. A gas sensing device substantially as hereinbefore described with reference to and as shown in Figures 4 and 5 of the accompanying drawings.
16. Any novel feature or combination of features disclosed herein.



The
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Application No: GB 9408383.9
Claims searched: 1 - 15

Examiner: D J Mobbs
Date of search: 20 June 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): G1N NBMH, NBMS, NBMT, NBPT

Int Cl (Ed.6): G01N 27/417, 27/419, 27/49

Other: NONE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0434085 A2 ULTRAKUST ELECTRONIC	1 - 7, 9, 14.
X	EP 0432649 A1 GTE LABORATORIES	1
X	US 4576705 TOYOTA CHUO KENKYUSHO	1

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